Collaborative Study of Soils Spiked with Volatile Organic Compounds

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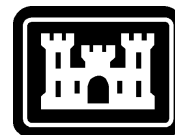
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Abstract

Vapor fortification is a method of spiking soils with volatile organic compounds (VOCs) that was recently developed for producing materials suitable for performance evaluation and quality assurance/quality control (QA/QC). Using this treatment method, soil subsamples enclosed in heat-sealed glass ampoules were distributed to 16 laboratories for a collaborative round-robin study. The sample sets consisted of duplicates of three different soils. Each soil subsample had been vapor-fortified with the following VOCs: trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben) and toluene (Tol). The laborator-ies were requested to report analyte concentration estimates for these four anal-ytes and any other detected organic compounds after performing a methanol extraction, purge-and-trap gas chromatography, mass spectrometry analysis. The results from the 12 laboratories that met all of the design criteria produced a range of relative standard deviations from 8.5 to 28.2%, with a pooled stan-dard deviation of less than 13%. The smallest range of consensus values was for Ben (pooled RSD = 9.0%), while the determination of TDCE showed the greatest overall uncertainty (pooled RSD = 20.3%). This round-robin effort confirmed that the use of vapor-fortified soils sealed in glass ampoules is a precise way of preparing and storing VOC-spiked soil subsamples.

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PREFACE

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INTRODUCTION

The wide use and subsequent improper disposal or unintentional release of petroleum products and chlorinated solvents has made volatile organic compounds (VOCs) our most common environmental hazardous waste problem (Plumb and Pitchford 1985). Despite the large number of vadose-zone soil samples routinely characterized for VOCs, no secondary reference soils are available for evaluating determinative accuracy, for quality assurance/quality control (QA/QC) among and within laboratories, or for method comparisons (Zarrabi et al. 1991). Currently the accuracy of soil VOC analyses relies on solution spike and recovery tests. One common practice is to add dilute methanol (MeOH) solutions containing the analytes of interest to samples just prior to analysis (Maskarinec et al. 1989). This method evaluates the determinative step but fails to address the extraction step by not allowing time for natural sorptive processes to occur and by introducing a carrier solvent (i.e., MeOH). Furthermore, this laboratory treatment method does not simulate the manner in which soils in the vadose zone are contaminated.

The accuracy of laboratory estimates of analyte concentrations in environmental samples initially depends on analytical calibration. Thereafter, accuracy is monitored during routine analyses of real samples by reference to results on accompanying QA/QC samples. For this system to work effectively, reference samples with accurately known analyte concentrations must be available in a stable form that mimics real samples. For VOCs in soils, the preparation and distribution of such materials is extremely difficult (Minnich and Zimmer, in press). In the absence of such reference materials, comparisons based on sample splits have frequently been used to address QA/QC issues. This practice is questionable for analyzing VOCs in soils because of problems associated with collection, handling, storage and spatial heterogeneity (Siegrist and van Ee 1993, Hewitt 1994a,b,c).

Vapor fortification offers a means of spiking soils that overcomes many of the shortfalls of previous methods (Jenkins and Schumacher 1987; Hewitt 1993, 1994d,e, in press; Hewitt et al. 1994). This method of soil spiking takes place over several days in a closed system by exposing individual subsamples of soils contained in open 1.0-mL glass ampoules to vapors of the VOCs of interest. After the vapor fortification treatment the ampoules are removed from the desiccator and quickly heat-sealed to prevent volatilization losses. Preparation by this treatment method is soil specific and is precise within and between batches, and analyte concentrations are stable at room temperature for holding periods exceeding 60

Table 1. Analyte concentrations (μg/g) established by headspace gas chromatography for vapor-fortified soil subsamples held at room temperature in sealed glass ampoules. This table is a continuation of the holding time results reported elsewhere (Hewitt 1994b).

Holding time	Compound			
(days)	TDCE*	Ben	TCE	Tol
Tampa Bay sediments (TB)				
28	8.0±0.3*	9.1±0.3	10±0.6	11±0.6
60	8.2±0.9	9.1±0.3	11±0.6	12±0.6
120	7.5±l.6	9.0±0.7	12±0.6	13±0.6
240	6.7±0.5	8.3±0.3	11±0.6	12±0.6
Rocky Mountain Arsenal soil (RMA)				
0	13±1.0[†]	15±0.6	16±0.6	22±0.6
30	13±0.6	14±0.6	16±0.6	20±0.6
60	13±0.6	15±0.0	17±0.6	22±2.5
119	12±0.6	13±0.0	17±0.0	20±0.0
210	12±0.6	13±0.0	16±0.0	19±0.6
Point Barrow Alaska soil (PBA)				
0	39±1.0[†]	38±0.6	59±1.7	68±2.1
30	38±1.7	38±1.7	56±2.9	66±1.5
60	36±1.5	37±0.6	56±0.6	66±5.8

* TDCE = trans-1,2-dichloroethylene; TCE = trichloroethylene; Ben = benzene; Tol = toluene.
† Mean and standard deviation (n = 3).

days (Table 1). These qualities made it possible for us to distribute subsamples fortified with VOCs for an interlaboratory study where both extraction and determinative accuracy were evaluated.

Sixteen laboratories were sent duplicate subsamples of three different soils, each vapor-fortified with trans-1,2-dichloroethylene (TDCE), trichoroethylene (TCE), benzene (Ben) and toluene (Tol). To demonstrate precision between preparation batches, each soil set consisted of subsamples that were independently fortified. Thirteen laboratories (App. A) submitted analyte concentration estimates for these soils, using Method 8240 of the SW-846 (U.S. Environmental Protection Agency 1986). This method of determination is based on methanol extraction purge-and-trap gas chromatography/mass spectrometry (PT/GC/MS) analysis. The results from 12 of these laboratories were used to establish consensus analyte concentrations for these soils after a statistical evaluation using Youden plots, laboratory ranking and Dixon's test (Youden and Steiner 1975, Dixon 1953). This report documents the round-robin design, the results (App. B), the statistical evaluation and our conclusions about the merits of VOC performance evaluation soil subsamples.

EXPERIMENTAL METHODS

Participating laboratories

Twenty-two laboratories were asked to participate in this round-robin study. Sixteen laboratories agreed to participate, of which 13 returned completed report forms after receiving and analyzing the VOC-fortified soil subsamples.

Preparation and distribution of test materials

Three soil matrices were used in this study. Two of these soils serve as reference matrices for the U.S. Army Environmental Center: a marine sediment from Tampa Bay, Florida (TB), and a composite soil from the Rocky Mountain Arsenal (RMA) in Denver, Colorado. The third soil was

Table 2. Characteristics of soils.

Characteristic	TB*	RMA	PBA
Organic carbon (%)	0.31	0.05	6.7
Clay (%)	< 5	NA	20.1

* TB = marine sediment, Tampa Bay, Florida.
RMA = Rocky Mt. Arsenal composite soil, Denver, Colorado.
 PBA = soil, Point Barrow, Alaska.
  NA = not available

from Point Barrow, Alaska (PBA). Clay and organic carbon concentrations for these soils are shown in Table 2.

In preparation for the vapor fortification treatment, the soils were air-dried overnight, sieved through a 30-mesh screen and mixed thoroughly. Forty individual subsamples were prepared for each soil type by transferring weighed quantities into 1.0-mL glass ampoules using a stainless steel spatula and plastic funnel. The PBA subsamples weighed to 1.50 ± 0.01 g, while the RMA soil and TB sediment subsamples weighed 2.00 ± 0.01 g. Different weights were chosen so that the volume of soil was consistent and filled only the body of the glass ampoule.

Vapor fortification was performed on batches of 20 subsamples of a given soil at a time so as to limit the exposure period while the ampoules were sealed. Each batch of soil-filled ampoules was placed in a 5.6-L desiccator with a dish of anhydrous $CaSO_4$. Following two days of desiccation, the $CaSO_4$ was replaced with an open 60-mL glass bottle containing 50 mL of a solution of the analytes of interest to start the fortification process. This solution was prepared by combining 25 mL of a MeOH stock solution (0.60 g of Tol, 0.59 g of TCE, 0.50 g of TDCE and 0.35 g of Ben diluted to 100 mL) with 25 mL of tetraethylene glycol dimethyl ether (tetraglyme). This equal-volume combination of MeOH and tetraglyme was found to be relatively insensitive to laboratory temperatures (17° to –24°C) and produced the most predictable and precise treatment levels for the solvents and solvent mixtures tested (Hewitt 1993).

After seven days of vapor fortification, the desiccator was opened and a 5-mm-diameter glass bead was rapidly placed on top of each ampoule, forming a temporary cap. Then, as quickly as possible, each ampoule was put in a metal tension clamp and the neck was heat-sealed using a propane plumber's torch. This operation took approximately 10 minutes from the time the desiccator was opened until all the ampoules were sealed. A sharp-pointed tip was created when sealing the ampoules to facilitate breaking when preparing for analysis. Details on the development of this procedure and its performance have been documented elsewhere (Hewitt 1993, 1994d,e, in press).

Each fortification batch and the sequence in which the individual ampoules were heat sealed were recorded. Sixteen sets, each consisting of six subsamples, were prepared. Each set contained one sample randomly selected from the first 16 samples in each of the six treatment batches. This

design allowed us to examine batch-to-batch precision, since duplicate samples were prepared in different desiccators. The design also permitted evaluation of intra- and interlaboratory analytical precision.

The sample packages distributed to each participating laboratory contained:
- Eight VOA vials (one extra);
- Seven sealed glass ampoules containing soil [three pairs (1 & 2) of vapor-fortified soils labeled A, B and C, and one blank soil labeled D for practicing the ampoule-breaking operation];
- One QA ampoule (VOA-2, Ultra Scientific) with certified concentrations of Ben, Tol and TCE* in MeOH; and
- Handling and analysis instructions and reporting forms.

Soil subsample and QA sample handling and analysis

It was imperative that the procedures used by each laboratory be as consistent as possible to minimize systematic errors. For this reason, very specific handling and analysis instructions were provided. Prior to analysis the laboratories were requested to calibrate their instrument for the analysis of TDCE, TCE, Ben and Tol over a range of at least 1 to 100 $\mu g/L$. Analyses of both the QA standard and the soil subsamples were to be performed within a single day and within one month of sample receipt. Between receipt and analysis the entire sample set was to be refrigerated (4°C). All analyses were performed by PT/GC/MS following the general guidelines of SW 846, Method 8240 for VOC concentrations greater than 1 $\mu g/g$ (U.S. Environmental Protection Agency 1986). The soil subsamples were first dispersed in MeOH; then a portion of the methanolic solution was combined with approximately 5 mL of water for PT/GC/MS analysis.

On the day of analysis, the analyst was requested to make a $1/20$ dilution of the QA standard provided, using the same MeOH that was to be used for extracting the soil subsamples. A 100-μL aliquot of the $1/20$ dilution was added to 4.90 mL of water and then transferred to a purge chamber. This QA standard was the first to be analyzed so that the analyst could check the instrumental calibration. If the results of this analysis were not within 20% of the certified concentrations for TCE, Ben and Tol, they were supposed to reanalyze the QA standard and/or consider recalibration before continuing.

To prepare a vapor-fortified soil for analysis, 20.0 mL of MeOH was added to one of the supplied VOA vials. Then an ampoule with its sealed tip pointing toward the bottom and representing one of the three soil subsample pairs, 1 or 2, which were to be distinguished throughout, was placed into the VOA vial. Once the VOA vial was capped, the ampoule was broken by hand shaking, to allow the soil to become dispersed. A practice soil subsample (D) was included to allow the analyst a chance to determine how hard to shake a VOA vial when breaking an ampoule filled with soil. We recommended that the analyst wear rubber gloves and that the strength of shaking be increased slowly and not increased further once the ampoule was broken. Our experience has shown that only a portion of the sealed tip has to be broken for the soil to be released. However, if, after two minutes of hand shaking, soil remained trapped in the ampoule, shaking was to be continued until complete dispersion resulted. The methanolic extracts were transferred after the soil had settled (approximately 20 minutes) by opening the VOA vial and withdrawing the specified aliquot with an appropriate syringe.

The ampoules marked A and B contained vapor-fortified TB sediment and RMA soil, respectively. A 50.0-μL aliquot of the 20.0-mL MeOH extraction solution was transferred with a 100-μL syringe to a 5.00-mL syringe containing 4.90 mL of water. To keep a constant volume of MeOH added to the purge-and-trap vessel, 50.0 μL of analyte-free MeOH was also added with a fresh syringe.

Ampoules marked C contained vapor-fortified PBA soil. A 10.0-μL aliquot of the 20.0-mL MeOH extraction solution was transferred with a 25-μL syringe to a 5.00-mL syringe containing 4.90 mL of water. To keep a constant volume of MeOH added to the purge-and-trap vessel, 90.0 μL of analyte-free MeOH was also added with a fresh syringe.

Data packages

Each laboratory was asked to provide the following results:
- Instrumental calibration for TDCE, TCE, Ben and Tol;
- Concentration estimates for TCE, Ben and Tol in the supplied QA standard, along with results for any other analytes detected, regardless of whether the instrument was calibrated for them; and
- Concentration estimates for TDCE, TCE, Ben,

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*A commercial standard containing TDCE was not available.

Tol and any other detected analytes, for each of the six fortified soil subsamples.

All analyte concentrations were reported in μg/mL. We converted these results to soil concentrations using the masses of the subsamples. In addition, each laboratory was asked to report the date of analysis and the model and manufacturer of their mass spectrometer, purge-and-trap instrument, purge-and-trap column, gas chromatograph and column.

RESULTS

Rationale for statistical tests

The primary purpose of this study was to demonstrate that soil samples could be reproducibly vapor fortified with VOCs and distributed to laboratories for various performance evaluation purposes. After careful inspection and the use of several statistical tests, a few extreme (outlier) values were excluded from the final analysis. Knowledge of the analytical system was used in reaching decisions to retain some results despite the presence of small but statistically significant systematic errors. Evaluation of collaborative test results always seems to require compromise to avoid excessive exclusions while preventing gross distortion that can be caused by a few extreme values. When a laboratory produces several outliers in the same direction, this is strong evidence of a large systematic error, and exclusion of that data is justified.

Examination of laboratory reports

Analytical results and sample analysis dates were first reviewed to detect any obvious problems. Laboratory 13 was unable to analyze the treated soil subsamples within the specified holding time due to instrument problems, so those data were omitted. The results were excellent for the analysis of the three analytes in the QA standard supplied with each sample set. The mean values for TCE, Ben and Tol differed from the certified concentrations by an average of only 2.8%. Relative standard deviations for the three analytes varied from 7.2 to 8.8% (Table 3).

All of the results provided by the 13 laboratories are given in Appendix B. Results for subsample A1 from laboratory 5 showed that two analytes were not detected, while the other two were abnormally low. It was concluded that the ampoule must not have been properly sealed. To maintain balance in the data array, both subsamples A1 and A2 from laboratory 5 were excluded. A very low recovery for the internal standard of subsample B2 from lab-

Table 3. Interlaboratory results for the certified QA standard (Volatiles Mix 2, Ultra Scientific).

Benzene (50.2 μg/mL certified)	
Mean	51.9
Std Dev.	3.8
RSD*	7.4%
Trichloroethylene (50.1 μg/mL certified)	
Mean	51.9
Std Dev.	3.8
RSD	7.2%
Toluene (50.1 μg/mL certified)	
Mean	50.8
Std Dev.	4.5
RSD	8.8%

* Relative standard deviation

oratory 16 was also noted, but the data were retained for further review.

Youden two-sample plots

Youden two-sample plots provide an excellent visualization of the relative amount of systematic error between laboratories compared to the amount of random error (Youden and Steiner 1975). Since the two batches of subsamples for each soil were prepared independently, we plotted the two concentration values from each laboratory against each other. Concentrations of all four analytes for a given soil were plotted on a single graph after adjusting the means for each analyte (by subtraction) to the mean of the analyte with the lowest concentration. This process leaves the absolute magnitude of the variations unchanged.

Figure 1 contains the soil C results prior to any data exclusion. In the presence of random error only, the points should form a circular array with approximately equal numbers of points in each of the four quadrants formed by the intersection of lines representing the means. Systematic error causes points to depart from this intersection of the means along a 45° line. Clearly, there is large systematic error for laboratories 3 and 12 for all four analytes, most likely due to calibration variations between laboratories. Although not shown here, similar patterns were observed for soils A and B.

If we exclude data from laboratories 3 and 12 and replot the data with revised means (Fig. 2), there is still a distinct elliptical pattern characteristic of a combination of random and systematic error. Instead of an equal number of points in each quadrant, the low-low quadrant contains 15 points, the high-high has 14, and the other two quadrants contain only 5 and 6 points. It is also
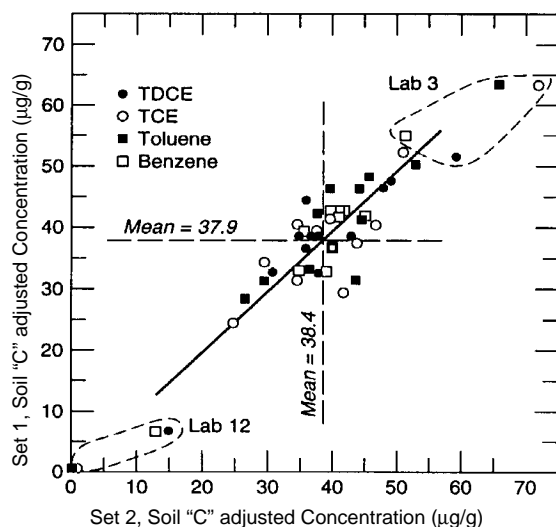
Figure 1. Youden two-sample plot for four analytes in soil C as reported by 12 laboratories. Concentrations of the 12 pairs of results for TDCE, TCE and Tol were adjusted to the same mean as Ben by subtracting 0.3, 18.4 and 23.4 µg/g, respectively, to permit plotting on a single graph.
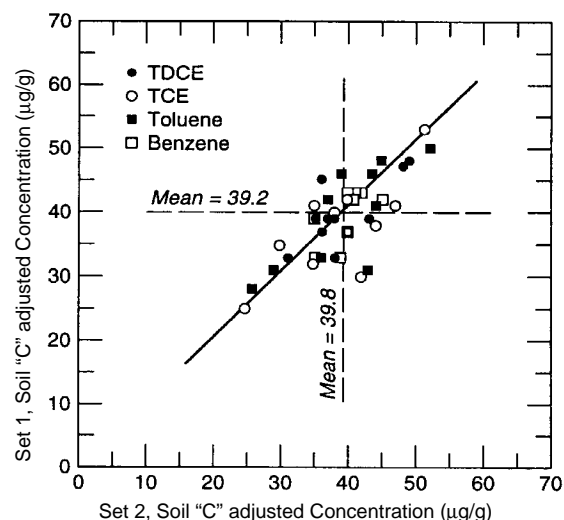
Figure 2. Youden two-sample plot for four analytes in soil C as reported by 10 laboratories (laboratories 3 and 12 excluded). Concentrations of the 10 pairs of results for TCE and Tol were adjusted to 39.5 µg/g (both TDCE and Ben had this mean) by subtracting 16.7 and 24.0 µg/g, respectively.

worth noting that the results for Ben cluster much more closely around the intersection of the means than any other analyte. Later precision estimates confirm that the most reproducible concentration estimates were for Ben.

Laboratory ranking test

Before excluding all results from laboratories 3 and 12, a ranking test was conducted (Youden and Steiner 1975). The laboratories were ranked for each analyte in each soil according to the means of the two batches. Thus, for each analyte in each soil, rank 1 was assigned to the laboratory with the highest concentration and so on to rank 12 for the lowest concentration. The final score for each laboratory was the sum of its ranks (Table 4). For 12 laboratories reporting 12 concentrations (3

Table 4. Results of laboratory ranking test.

Laboratory	Sum of 12 ranks	Laboratory	Sum of 12 ranks
1	110.5	9	67
3	17*	10	88.5
4	85	11	56.5
5	118.5[†]	12	135.5*
7	84.5	15	68
8	39[†]	16	67

* The 95% confidence limit scores for a random process are 44 and 112. Laboratories 3 and 12 are strongly biased.
† Laboratories 5 and 8 also show significant bias but the results were not excluded.

soils × 4 analytes), the lowest possible score was 12 and the highest was 144. For completely random data, 5% two-tail probability limits are 44 and 112. Laboratory 3 (with a score of 17) and laboratory 12 (with a score of 135.5) exhibited pronounced systematic error, justifying their exclusion. Calibration errors were likely the cause of this problem.

Because of the elliptical pattern of Figure 2, it was not too surprising that two more laboratories were also outside of the limiting scores (but only slightly). As with 3 and 12, one was out on the high side and one was out on the low side. However, we were reluctant to exclude these data given the relatively small number of laboratories. Retention of these results did not significantly alter mean concentration estimates but it did increase the confidence limits around the means.

Dixon's test

This test uncovers individual stray results, i.e. it is sensitive to values that fall outside the range expected for randomly distributed data (Dixon 1953). Only one result was classified as an outlier ($\alpha = 0.05$) using this test, and that result was barely excludable, so it was retained.

Range test on duplicates

A basic premise of analysis of variance (ANOVA) is homogeneity of variances. A range test was conducted on the duplicate values from batches (Youden and

Table 5. Summary of edited results for VOCs in the three soils.

Soil A, Tampa Bay sediments	TDCE		TCE		Ben		Tol	
	A1	A2	A1	A2	A1	A2	A1	A2
Batch means (µg/g)	6.73	6.04	8.84	8.32	7.56	6.92	10.5	9.93
Overall mean* (µg/g)	6.39		8.58		7.24		10.2	
Std. dev. (µg/g)	1.80		0.85		0.71		0.95	
RSD (%)[†]	28.2		10.0		9.8		9.3	
95%CL**(µg/g)	5.5–7.3		8.2–9.0		6.8–7.6		9.7–10.7	

Soil B, Rocky Mtn. Arsenal	TDCE		TCE		Ben		Tol	
	B1	B2	B1	B2	B1	B2	B1	B2
Batch means (µg/g)	11.0	11.1	15.5	15.6	14.1	14.1	19.7	19.0
Overall mean* (µg/g)	11.0		15.6		14.1		19.4	
Std. dev. (µg/g)	1.9		1.7		1.2		1.8	
RSD (%)[†]	17.0		10.8		8.5		9.5	
95%CL**(µg/g)	10.1–11.9		14.8–16.4		13.5–14.7		18.5–20.3	

Soil C, Pt. Barrow, Alaska	TDCE		TCE		Ben		Tol	
	C1	C2	C1	C2	C1	C2	C1	C2
Batch means (µg/g)	39.1	39.9	55.7	56.7	39.2	39.8	63.6	63.4
Overall mean* (µg/g)	39.5		56.2		39.5		63.5	
Std. dev. (µg/g)	5.4		7.6		3.5		7.7	
RSD (%)[†]	13.6		13.5		8.8		12.2	
95%CL** (µg/g)	37.0–42.0		52.6–59.8		37.9–41.1		59.9–67.1	

 * There were no significant differences in batch means (α = 0.05); batches were combined.
 † Relative standard deviation.
 ** 95% Confidence limits on overall means.

Steiner 1975). The ranges were homogeneous except for the laboratory 16 results for soil B, where three of the four analytes were outside of acceptable limits (α = 0.05). Since subsample B2 had been flagged earlier due to a very low recovery of the internal standard, soil B results for laboratory 16 were excluded.

Edited data set

At the conclusion of these tests, we were left with complete data sets for nine laboratories for soils A and B and ten laboratories for soil C. Laboratories 3, 12 and 13 were excluded for all soils, laboratory 5 was excluded for soil A, and laboratory 16 was excluded for soil B.

The ANOVA confirmed that significant laboratory differences remained (α = 0.05), along with a small but statistically significant interaction between laboratories and samples. This situation was not unexpected in view of our earlier decision to retain two laboratories with significant systematic errors based on the ranking test. We believe that these small systematic errors are detectable because of the excellent precision obtained. Furthermore, we feel that no further exclusions are necessary or desirable. A summary of the edited results appears in Table 5.

One important conclusion from these results is that none of the batch means differed significantly from its replicate (α = 0.05). In fact, only Ben in soil A yielded a *t* statistic that even approached the critical value for significance. This finding suggests that batches of subsamples can be reproducibly prepared over time using a given soil and a given fortifying solution of VOCs. Further evidence for the predictability of the procedure is seen in Table 6, where analyte percentages relative to the total of the four analytes are computed for each soil. The percentages are quite consistent despite substantial differences in the clay and organic matter content of the soils, which suggests

Table 6. Percentages of each spiked analyte relative to the total of the four analytes in each soil.

	Percent of each analyte relative to the total			
Analyte	Soil A	Soil B	Soil C	Average
TDCE	19.7	18.4	19.9	19.3
TCE	26.5	25.9	28.3	26.9
Ben	22.3	23.4	19.9	21.9
Tol	31.5	32.3	31.9	31.9
Total	100.0	100.0	100.0	100.0

that the composition of the fortifying solution is paramount. With respect to the potential for volume production of subsamples for distribution, these observations are reassuring.

In the absence of significant differences in batch means, all values for a given analyte in a given soil were combined to yield an overall mean, standard deviation, percent relative standard deviation and 95% confidence limits around the mean (Table 5). With the exception of TDCE, which is the most volatile of the analytes tested, the RSDs and 95% confidence limits are excellent, despite the residual systematic error known to remain. Although the larger uncertainties associated with TDCE were not unexpected, the results are still quite good for the analysis of VOCs in a porous matrix.

DISCUSSION

This study shows that laboratories following the procedures outlined in Method 8240 (U.S. Environmental Protection Agency 1986) are capable of reliably determining VOC concentrations in either spiked MeOH or soil materials that have been designed for performance evaluation. The comparison of the pooled RSDs for the analytes common to both the supplied QA MeOH solvent-based standard and the soil subsamples (Ben, Tol and TCE) resulted in values of 7.8% and 10.4%, respectively. The differences between these values are minor, considering that the QA samples were distributed with specified analyte concentrations, whereas analysts were not informed of the concentrations present in the soil subsamples, and the latter required an extraction step prior to analysis (Hewitt et al. 1994).

Unfortunately this degree of determinative uncertainty cannot often be extended to cover estimates of VOC concentrations in vadose-zone soil subsamples. This is because vadose-zone soils are usually transferred from the field to a laboratory as bulk samples. This requires that the sample matrix be handled at least twice prior to analysis: once when the bulk sample is placed in a shipping or storage bottle and again when a subsample is removed for analysis. During these handling operations the VOC concentrations can become significantly reduced due to volatilization losses (Urban et al. 1989, Siegrist and Jenssen 1990, Siegrist and van Ee 1993, Hewitt 1994a,c). Also, while being held at 4°C, analyte biodegradation has been shown to cause rapid reductions in the concentration of some VOCs (Hewitt 1994b). These losses were avoided here by eliminating the need to transfer or expose soil subsamples to the atmosphere and by desiccating the soil prior to spiking, thereby minimizing biological activity.

The availability of reliable QA/QC soil subsamples for the analysis of VOCs will allow us to judge laboratory performance in a matrix that is consistent with vadose-zone samples. Moreover, of perhaps even greater importance would be the use of such materials for comparing different methods of analysis. Currently site assessments are carried out by a variety of analytical sample preparation and collection methods, including passive and active soil vapor, thermal desorption, solvent extraction and water-based static and dynamic extraction. Furthermore, several detection systems are available for quantification. The opportunity to use performance evaluation soil subsamples for correlations between these analytical methods would broaden our understanding of their capabilities and applicability.

CONCLUSION

The results from this round-robin study show that vapor fortification treatment and glass ampoule confinement is a relatively simple, cost-effective means to produce reliable, precise and reproducible soil subsamples spiked with VOCs with good concentration stability and ease of distribution for use as QA and QC materials. These features also make vapor-fortified soils suitable for assessing the precision and accuracy of procedures for sample preparation (extraction) and analysis (determination).

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APPENDIX A: LIST OF THE 13 LABORATORIES
THAT RETURNED COMPLETED DATA PACKAGES

Laboratories listed in random order.

U.S. Army Corps of Engineers
New England Division Laboratory
Hubbardston, Massachusetts 01452
William Saner

Data Chem Laboratories
960 LeVoy Drive
Salt Lake City, Utah 84123
Lawrence S. Hall

Midwest Research Institute
425 Volker Blvd
Kansas City, Missouri 64110
Roger Rowan, Analyst; Don D. Gay, Director

U.S. Army Corps of Engineers
Missouri River Division Laboratory
420 South 18th Street, Omaha, Nebraska 68102
Thomas G. Leuschen, Analyst; Dave Splichal,
    Supervisor

Lockheed Environmental Systems and Technology
    Company
P.O. Box 93478
Las Vegas, Nevada 89193
Jeff Jeter, Analyst; Marti Minnich, Supervisor

U.S. Army Engineer Waterways Experiment
    Station
3909 Halls Ferry Road
Vicksburg, Mississippi 39180
Bobby Jones, Analyst; Richard A. Karn, Team
    Leader; Karen F. Myers, QA/QC Officer;
    Ann B. Strong, Group Chief; Linda K. Stevenson,
    Technician

U.S. Army Corps of Engineers
Ohio River Division Laboratory
11275 Sebring Drive, Cincinnati, Ohio 24534
Kerry R. Nusekabel, Analyst; John Adams,
    Supervisor

ESE Laboratory
P.O. Box ESE
Gainsville, Florida 32602
Gregory G. Lamb, Analyst; Mike Winslowe,
    Supervisor

Rust Geotech
PO Box 1400
Grand Junction, Colorado 81502
Gretchen Loshbaugh, Analyst; Steve Donvon,
    Supervisor

EPA Region 1 Service Division
60 Westview Street
Lexington, Massachusetts 02173
Sten Heller, Analyst; Suresh Srivasta and Joseph
    Montanaro, EPA contacts; Joseph Montanaro,
    Data Reviewer

Enviro-Tech Research
777 New Durham Rd.
Edison, New Jersey 08817
David Sherman, Analyst; Mike Urban, Supervisor

Los Alamos National Lab
Los Alamos, New Mexico 07545
Don Dale and Matthew Monagle, Analyst; Chris
    Leibman, Supervisor; Peggy Gautier, QA&DM
    Section Leader

U.S. Army Cold Regions Research and Engineer-
ing
    Laboratory
72 Lyme Road
Hanover, New Hampshire 03755
Chad Pidgeon, Analyst; Mike Reynolds,
    Supervisor

APPENDIX B: UNEDITED ANALYTE CONCENTRATIONS (μg/g) DETERMINED BY COLLABORATORS

Lab	A1	A2	B1	B2	C1	C2	QA*	Lab	A1	A2	B1	B2	C1	C2	QA*
TDCE								**TCE**							
1	5.4	4.0	9.9	10.9	33	31		1	7.6	6.5	12.6	13.3	43	43	47.0
2	6.2[b]	6.2[b]	13.8[b]	12.2[b]	42[b]	39[b]		2	9.2[b]	10.4[b]	18.8[b]	16.0[b]	61[b]	52[b]	51.1[b]
3	8.1[a]	6.6[a]	13.4[a]	15.3[a]	52[a]	59[a]		3	10.2[a]	9.8[a]	20.4[a]	22.1[a]	82[a]	90[a]	54.9
4	6.0	4.5	9.5	10.6	37	36		4	8.8	8.0	14.2	14.9	60	58	50.7
5	ND[c]	3.7[c]	10.2	9.3	39	43		5	1.9[c]	7.7[c]	14.6	14.0	50	53	46.2
7	5.5	6.5	10.5	10.9	45	36		7	8.2	8.1	14.9	14.8	59	53	50.8
8	5.3	6.0	10.5	10.9	39	38		8	10.1	9.0	18.1	19.2	71	69	55.3
9	11.1	9.4	16.0	15.6	47	48		9	9.3	9.3	17.5	15.6	56	62	52.5
10	6.0	6.7	9.7	11.0	33	38		10	9.1	8.7	14.5	16	48	60	NR
11	5.3	6.3	11.7	10.3	39	37		11	8.9	9.4	16.6	16.1	59	65	55.6
12	2.7[a]	4.7[a]	11.0[a]	10.0[a]	7.3[a]	15[a]		12	4.0[a]	6.2[a]	14.0[a]	13.0[a]	11[a]	19[a]	47.7
15	6.8	5.3	11.5	9.4	39	35		15	9.3	8.4	16.3	16.3	58	56	53.0
16	9.2	5.7	19.7[a]	11.5[a]	48	49		16	8.3	7.5	16.7[a]	11.5[a]	53	48	57.2
Ben								**Tol**							
1	9.2	6.4	13.7	14.8	37	40	51.9	1	8.8	8.5	17.4	18.3	52	50	47.4
2	7.4[b]	8.3[b]	23.8[b]	15.1[b]	43[b]	38[b]	50.9[b]	2	10.9[b]	13.6[b]	25.2[b]	23.2[b]	70[b]	61[b]	51.6b
3	8.3[a]	7.5[a]	17.0[a]	18.6[a]	55[a]	51[a]	55.0	3	11.6[a]	10.9[a]	23.9[a]	24.9[a]	87[a]	89[a]	54.9
4	7.6	6.5	13.2	13.9	42	41	50.8	4	10.6	9.6	18.7	19.6	72	69	49.8
5	ND[c]	5.6[c]	12.4	11.5	33	35	45.2	5	4.3[c]	9.1[c]	19.6	18.0	57	60	48.9
7	6.5	6.8	13.6	13.9	43	40	49.3	7	9.9	10.0	19.1	18.7	70	63	48.1
8	7.8	7.5	15.7	16.0	43	42	55.9	8	12.1	11.5	23.6	20.3	74	76	54.6
9	7.1	6.8	15.2	13.4	37	40	51.8	9	9.9	9.1	16.9	15.8	55	53	43.4
10	7.0	6.9	12.7	14.1	33	39	NR	10	10.8	10.0	19.1	20.1	55	67	NR
11	7.0	7.6	15.5	15.0	42	45	53.1	11	9.8	10.2	20.7	20.3	65	68	55.4
12	3.0[a]	4.8[a]	12.0[a]	12.0[a]	6.7[a]	13[a]	46.6	12	4.6[a]	6.8[a]	17.0[a]	17.0[a]	11[a]	20[a]	45.9
15	7.4	6.9	14.5	14.1	39	35	53.0	15	11.5	10.8	22.2	20.3	70	67	52.6
16	8.4	6.9	13.3[a]	12.6[a]	43	41	58.1	16	10.9	9.7	24.8[a]	15.7[a]	66	61	57.2

* QA standard.
a Outlier.
b Analysis performed outside of specified holding time.
c Ampoule leaked, subsample set omitted.
NR No result provided.
ND Not detected.

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13. ABSTRACT (*Maximum 200 words*)

Vapor fortification is a method of spiking soils with volatile organic compounds (VOCs) that was recently developed for producing materials suitable for performance evaluation and quality assurance/quality control (QA/QC). Using this treatment method, soil subsamples enclosed in heat-sealed glass ampoules were distributed to 16 laboratories for a collaborative round-robin study. The sample sets consisted of duplicates of three different soils. Each soil subsample had been vapor-fortified with the following VOCs: trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben) and toluene (Tol). The laboratories were requested to report analyte concentration estimates for these four analytes and any other detected organic compounds after performing a methanol extraction, purge-and-trap gas chromatography, mass spectrometry analysis. The results from the 12 laboratories that met all of the design criteria produced a range of relative standard deviations from 8.5 to 28.2%, with a pooled standard deviation of less than 13%. The smallest range of consensus values was for Ben (pooled RSD = 9.0%), while the determination of TDCE showed the greatest overall uncertainty (pooled RSD = 20.3%). This round-robin effort confirmed that the use of vapor-fortified soils sealed in glass ampoules is a precise way of preparing and storing VOC-spiked soil subsamples.

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